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Contract Nonr-4756(07)

Task No. NR 015-816

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in the Lowest Triplet State of Pyrazine at 1.6°K

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Prepared for: Excitons, Magnons and Phonons in Molecular Crystals,
A. B. Zahlan, Editor; Cambridge University Press, 1968
(Proceedings of International Symposium, Beirut, 1968)

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February, 1968

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UCLA Contribution Number 2091.

ABSTRACT

The different mechanisms proposed for the spin lattice relaxation process of a paramagnetic impurity in ionic crystals are briefly summarized. The decay characteristics of the pyrazine phosphorescence in cyclohexane and benzene matrices at 1.6°K and its temperature dependence can best be explained if competition between the spin lattice relaxation process between the triplet sublevels and the radiative process from one of the sublevels of pyrazine is invoked. Spin polarization in the ${}^3B_{3u}^{n,\pi^*}$ state of pyrazine at 1.6°K is achieved by the selection rules imposed on the intersystem crossing process, ${}^1B_{3u}^{n,\pi^*} \rightsquigarrow {}^3B_{1u}^{n,\pi^*} (\tau_y)$, followed by the fast internal conversion process ${}^3B_{1u}^{n,\pi^*} (\tau_y) \rightsquigarrow {}^3B_{3u}^{n,\pi^*} (\tau_y)$. The latter sublevel (τ_y) of the ${}^3B_{1u}^{n,\pi^*}$ state is the emitting sublevel. This scheme is found to explain the observed temperature effects on the decay characteristics as well as the unique phosphorescence polarization along the N...N axis of the pyrazine molecule. Limits on the spin lattice relaxation time (T_1), on the lifetime of the $T_1 \rightsquigarrow S_0$ radiationless process and on the radiative lifetime of phosphorescence from the τ_x and τ_z sublevels of the ${}^3B_{3u}^{n,\pi^*}$ state of pyrazine at 1.6°K are determined. The effect of the magnetic field on the decay curve is demonstrated, and briefly described.

INTRODUCTION

The mechanisms involved in the spin lattice relaxation process of a paramagnetic impurity in an ionic solid have been carefully examined both experimentally and theoretically.⁽¹⁾ In 1932, Waller⁽²⁾ proposed a mechanism in which the phonon field of the lattice vibrations modulates the magnetic dipole-dipole interaction and thus introduces a time dependency into the interaction which induces spin relaxation. This mechanism is found not to explain the observed temperature and magnetic field effects on the relaxation process. Heitler and Teller⁽³⁾ indicated that the modulation of the electric field by lattice vibrations could modulate the electron orbital motion. Since the latter is coupled to the spin motion via spin orbit coupling, time dependence is then felt by the spin system which would cause spin relaxation. Van Vleck⁽⁴⁾ and others⁽¹⁾ have subsequently developed the theory for this mechanism. The direct process prevails at low temperatures and involves the exchange of the spin quantum with one phonon. This process is found to have a spin relaxation time T_1 which is inversely proportional to the absolute temperature (T). The Raman process in which the spin system absorbs a quantum of one frequency and scatters that of another is important at higher temperatures. This process is found to give a relaxation time T_1 , which is proportional to T^{-7} (or T^{-9}). A third mechanism is found to account for the relaxation process in systems having crystal field splitting Δ less than the maximum phonon energy. This mechanism involves the simultaneous absorption of a phonon of energy δ_1 and the emission of another of energy $\delta_1 + \delta$ along with spin flip from one spin level to a lower one having a separation of δ . Such a process is found⁽⁵⁾ to have a spin lattice relaxation time $T_1 \propto e^{-\Delta/kT}$.

In any spin-relaxation rate experiment, one is actually measuring a sum of two rates:

1. The spin lattice relaxation rate and
2. The lattice-bath relaxation rate.

Only if the latter process is very fast compared to the first one would the measured relaxation rate correspond to the spin lattice relaxation process. At very low temperatures, the lattice-bath relaxation might be slow and the observed relaxation time τ_b (which is not a measure of the spin lattice relaxation time alone) is found to be proportional to $1/T^2$ (the case of phonon bottleneck).

Spin lattice relaxation processes of a spin impurity in molecular crystals have not as yet been carefully investigated. The presence of spin system in the ground state of molecular crystals is not too common. The triplet state, however, can offer a method of introducing unpaired spins in molecular crystals. It would be interesting to determine T_1 in molecular crystals, compare it with that observed in ionic crystals, and examine the importance of the above mechanisms in the process of spin lattice relaxation in molecular crystals. In all the above mechanisms, the relaxation time is found to be inversely proportional to the square of both the orbital-lattice intersection energy (H_{ol}) and the spin orbit interaction (H_{so}). Since the binding in ionic crystals is stronger than in molecular crystals, the interaction between the lattice and the orbital motion of the valence electrons is expected to be stronger in the former than in the latter. Furthermore, the impurities generally used in ionic crystals have atomic numbers that are greater than those of the atoms of organic molecules (carbon, hydrogen, nitrogen and oxygen). Spin orbit interaction in impurities used in ionic crystals is thus expected to be larger than in paramagnetic impurity

molecules dissolved in molecular crystals. Therefore due to difference in the size of H_{ol} and H_{so} , it is expected that, for the same mechanism and the same temperature, inorganic systems would have shorter spin lattice relaxation times than molecular impurities in molecular crystals. It would be interesting to examine the effects of the other factors that enter into the expression for the lattice relaxation time, e.g., the phonon density, the phonon occupation number and, in particular, the velocity of sound.

In the following section, results are presented for the change of the decay characteristics of pyrazine phosphorescence in cyclohexane and benzene matrices upon changing the temperature and applying a magnetic field. A scheme is presented in which spin polarization is accomplished by electronic excitation of pyrazine followed by a highly selective intersystem crossing process. This scheme, and the assumption that spin lattice relaxation times are slower than the radiative lifetime from one of the lowest triplet sublevels below 10°K, are found to explain the temperature effects, the magnetic effects, the unique polarization of the phosphorescence as well as the observed numerical radiative lifetime at temperatures for which complete equilibration between the three triplet sublevels is accomplished.

DECAY CHARACTERISTICS OF PYRAZINE PHOSPHORESCENCE AT LOW TEMPERATURES

It is well known⁽⁶⁾ that the pyrazine phosphorescence in rigid glasses has a lifetime of ~20 millisecon at 77°K. The quantum yield is known to be ~0.5 and the observed lifetime is believed to be mostly radiative. The calculated lifetime, using only one direct spin orbit coupling scheme, $^3B_{3u} \xleftrightarrow{S.O.} ^1B_{1u}$, is found⁽⁷⁾ to be in reasonable agreement with the observed lifetime. In cyclohexane or benzene matrix, the phosphorescence of pyrazine is found to be exponential with only one lifetime of 18 milliseconds at 77°K. At 1.6°K, a nonexponential decay is observed which can be resolved into three exponential lifetimes: 6, 130 and 400 millisecon. At 4.2°K, three lifetimes can be resolved: 6, 60 and 320 millisecon. Between 4.2-10°K, the decay is rather nonexponential and above 10°K, the decay becomes exponential with only one lifetime, 18 millisecon (the same lifetime observed at 77°K).

A number of possibilities can be proposed to account for the above results. The observed effect of temperature can be due to temperature effects on the $S_1 \rightsquigarrow T_1$ intersystem crossing process, on the spin lattice relaxation process, on the $T_1 \rightsquigarrow S_0$ intersystem crossing process, or on the radiative processes from the different triplet sublevels to the ground state. If the spin lattice relaxation process and the internal conversion processes among the triplet manifold are faster than the radiative processes from the sublevels of the lowest triplet state (to the ground state), it can easily be shown that changes of the rates of all the other processes mentioned can only change the intensity and/or the lifetime of an exponential decay.

The presence of a nonexponential decay between 1.6 and 10°K (which might be a composite of three unimolecular decays) can best be explained by emission either from different molecules or from different sublevel(s)

of one type of molecule in which the spin lattice relaxation process between the spin sublevels is slow compared to the radiative lifetime. The first possibility can be eliminated on two accounts: 1. It cannot explain the continuous change of the characteristics of the decay from nonexponential below 10°K to exponential above this temperature, and 2. The absence of a decay with lifetime of 18 millisecc (i.e., that of pyrazine) in the 1.6 - 10°K is difficult to explain. This leaves the possibility of a competition between the radiative process and the spin lattice relaxation process as a strong candidate to explain the observed effects of temperature on the decay characteristics of pyrazine phosphorescence at low temperatures. A number of observations have recently been reported which were successfully explained in terms of a competition between the spin lattice relaxation and the radiative lifetime of aromatic hydrocarbons (which is one thousand times longer than that for pyrazine). The modulation of the phosphorescence intensity by saturating the ESR transitions of the triplet state,⁽⁸⁾ the observation of r.f. stimulated emission instead of absorption when the resonance condition is met for the triplet spin sublevels,⁽⁹⁾ and the effect of magnetic field on the phosphorescence decay⁽¹⁰⁾ are all examples reported and explained as described.

The effect of magnetic field on the decay of the pyrazine phosphorescence in benzene matrix at 1.6°K is shown in Fig. (1) during its fast decay period. The main results can be summarized as follows:

1. At 4.82 K-gauss, the decay can be resolved into three unimolecular decays, with lifetimes of 12, 30 and 120 millisecc. Each of the three unimolecular decays can be fitted well to an exponential curve over 4.2, 8.2 and 3.4 lifetimes for the short, medium and long lived components, respectively.

2. The lifetimes of the different components depend on the strength of the magnetic field in a rather complex manner.

3. The magnetic field has no effect on the decay of the pyrazine phosphorescence at 77°K, where a single exponential decay is observed.

Spin Polarization and Spin Lattice Relaxation

The temperature dependence experiments might be explained using the scheme shown in Fig. (2)* for energy degradation. Following the absorption process, the excited pyrazine molecule is deactivated to the zero point level of the lowest ${}^1B_{3u}^{n,\pi^*}$ state in $\sim 10^{-12}$ sec. This is followed by the intersystem crossing process $B_{3u}^{n,\pi^*} \rightsquigarrow B_{3u}^{\pi,\pi^*}$ (where the symmetry species here represent those for the total(space x spin) wavefunction). This corresponds to a radiationless transition between states having $B_{3u}^{n,\pi}$ and $B_{1u}^{\pi,\pi}$ as the symmetry of their spatial functions and A_g (singlet) and $B_{2g}(\tau_y)$ (triplet) as their spin functions, respectively. This is the most probable intersystem crossing process in pyrazine,⁽¹¹⁾ because of its strong first order spin orbit interaction as well as its relatively large vibration overlap integral [as compared to the other alternative processes ${}^1B_{3u}^{n,\pi^*} \rightsquigarrow {}^3B_{3u}^{n,\pi^*}$ (or ${}^3B_{2g}^{n,\pi^*}$)].

In the ${}^3B_{1u}^{\pi,\pi^*}$ state, the two electrons have the spin function τ_y of symmetry B_{2g} , i.e., the spin is in the y-direction in the molecular framework. The transition ${}^3B_{1u}^{\pi,\pi^*} \rightsquigarrow {}^3B_{3u}^{n,\pi^*}$ is an internal conversion process and takes place in $\sim 10^{-11}$ sec, which is a short time compared to the spin lattice time, T_1 , at this temperature. Thus the molecule is found in the ${}^3B_{3u}^{n,\pi^*}$ state with the spin lined up in the y-direction, i.e., the excitation by

* The N...N axis is taken to be the z-axis (B_{1u}), the other in-plane axis is taken as the y-axis (B_{2u}), and the axis normal to the molecular plane as the x-axis (B_{3u}).

absorption has resulted in a spin polarization in y-direction in the molecular framework. Whether the emission will result only from the τ_y sublevel of the triplet state or from the others depends mainly on the magnitude of the spin lattice relaxation time (T_1) relative to the radiative lifetime from the τ_y sublevel to the ground state. In pyrazine, the triplet sublevel τ_y of the $^3B_{3u}^{n,\pi^*}$ strongly couples to the $^1B_{1u}^{n,\pi^*}$ by first order spin orbit perturbation to give rise to the observed N...N - polarized phosphorescence.^(12,13) Thus the sublevel which is populated as a result of the radiationless selection rules is the one that has the strongest radiative transition probability. The observed radiative lifetime of the $B_{3u}^{n,\pi^*}(\tau_y) \rightarrow ^1A_g$ is thus 6 millisecon (not 18 millisecon as has been previously assumed). It should be pointed out that this value is in better agreement with the predicted⁽⁷⁾ value of one millisecon.

A few of the molecules will have modes of deactivation different from the one described above, and would thus end up in the τ_x and τ_z sublevels of the $^3B_{3u}^{n,\pi^*}$ state. They could return to the ground state by a direct radiative process, via the τ_y sublevel after undergoing spin lattice relaxation, or by the nonradiative $T_1 \rightarrow S_0$ process. If they are deactivated by radiation via the τ_y sublevel, the observed medium and long lifetimes thus measure the spin lattice relaxation times for the processes $\tau_x \rightarrow \tau_y$ and $\tau_z \rightarrow \tau_y$. If this is the case, then an upper limit for the other processes can be set. The lifetimes of the $T_1 \rightarrow S_0$ radiative and nonradiative processes from the τ_x and τ_z sublevels are thus longer than 120 and 320 millisecon at 1.6°K. The spin lattice relaxation time at 1.6°K in this system would then have the value of 0.1 - 0.3 seconds, which is not far from the value observed for many ionic systems at this temperature.⁽¹⁵⁾

According to this mechanism, phosphorescence is emitted mostly from one sublevel, (τ_y), with a radiative lifetime of 6 millisecc. As the temperature increases, the spin lattice relaxation time decreases and a competition between radiation from τ_y and relaxation between the three sublevels takes place. Above 10°K, the relaxation rate exceeds that of the radiation from τ_y . Thus the population of the molecules in sublevel τ_y is in thermal equilibrium with those in the other sublevels. The observed lifetime, k , is given by:

$$k = \sum_{i=1}^3 k_i n_i$$

where k_i is the radiative rate constant of sublevel τ_i ($i = x, y, z$) and n_i is its fraction population. At thermal equilibrium and at relatively high temperature $n_i \approx 1/3$. If the radiative rate constants from the sublevels τ_x and τ_z are neglected as compared to that from the sublevel τ_y , the observed lifetime above 10°K should be $= 1/3 \times 1/6 = 18 \text{ millisecc}^{-1}$, as observed.

The above mechanism accounts for:

1. The change in the characteristics of the decay at low temperatures.
2. The unique polarization of the pyrazine emission, as well as the polarization direction.
3. The numerical value of the observed lifetime at temperatures above 10°K.

The effect of magnetic field can be qualitatively mentioned. The fact that magnetic field affects the decay characteristics is a strong indication that the phenomenon is connected with the paramagnetic state (the triplet state). The field can have effects on the spin lattice relaxation process, as is known for inorganic systems. Of course, the three observed decays in the presence of the field are from levels that are themselves mixtures

of τ_x , τ_y and τ_z . A more careful study of the field dependence, in particular for pyrazine molecules in single crystals, is now in progress.

Assuming that the medium and long lifetimes reflect spin lattice relaxation times, the observed lifetimes at 1.6°K and 4.2°K might suggest the following conclusions:

1. The medium lifetime decreases from 130 to 60 millisecc as the temperature increases from 1.6 to 4.2°K. This behavior suggests the importance of the direct process as a mechanism for the relaxation involving this level.
2. The long lifetime decreases from 400 to 320 millisecc upon changing the temperature from 1.6 to 4.2°K. This change cannot be explained by any of the mechanisms discussed in the introduction. This might reflect a major difference between the ionic and molecular solids, or else might indicate that the observed long lifetime does not correspond to the spin lattice relaxation time.
3. The fact that the medium and long lifetimes behave differently upon changing temperature might suggest that the emitting sublevel, τ_y , is not centrally located in between τ_x and τ_z .

Further work on this and related systems is now in progress and is aimed at the examination of the exact mechanisms at different temperature ranges. Experiments are now contemplated in which the zero field splitting of the triplet state of pyrazine (which is not yet known) is determined optically by double resonance techniques.

ACKNOWLEDGEMENT

M. A. El-Sayed would like to thank the John Simon Guggenheim Foundation for their partial financial assistance during his sabbatical year (1967-1968), the faculty of the Chemistry Department at the American University of Beirut for their warm hospitality and Professor A. B. Zahlan for making his laboratory facilities available to the author, as well as for many stimulating discussions. The authors wish to thank the Office of Naval Research for their financial support of the experimental part of this research.

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FIGURE CAPTIONS

Figure 1. The effect of 4.8 k-Gauss magnetic field on the decay of pyrazine phosphorescence in benzene matrix at 1.6°K. Horizontal axis represents time (5 msec/div.) and the vertical axis is a linear relative intensity scale. The decay curve at bottom is recorded in the absence of the magnetic field, whereas that on top is that in the presence of the field. The apparent increase in lifetime on the application of the field is actually a result of an increase in the lifetime of the short lived component and a decrease in the lifetimes of the other two long lived components of the decay.

Figure 2. Spin polarization and phosphorescence following the direct absorption in pyrazine at temperatures for which the spin lattice relaxation is slower than the phosphorescence as well as the internal conversion processes. The different spin sublevels of the ${}^3B_{1u}^{\pi,\pi^*}$ and ${}^3B_{3u}^{n,\pi^*}$ triplet states are drawn arbitrarily in the order of increasing energy: $\tau_x(B_{3g})$, $\tau_y(B_{2g})$ and $\tau_z(B_{1g})$.

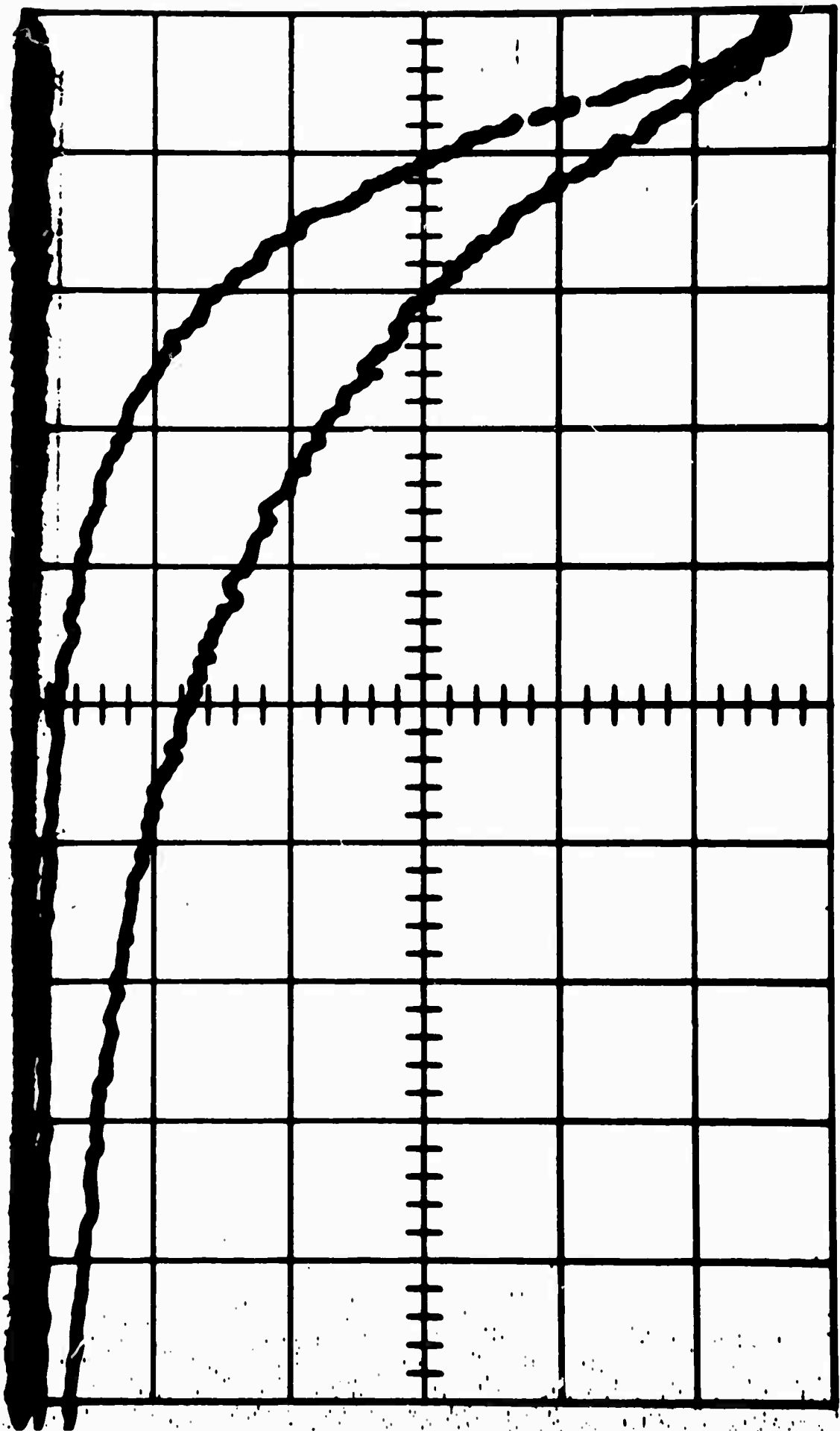


Fig. 1

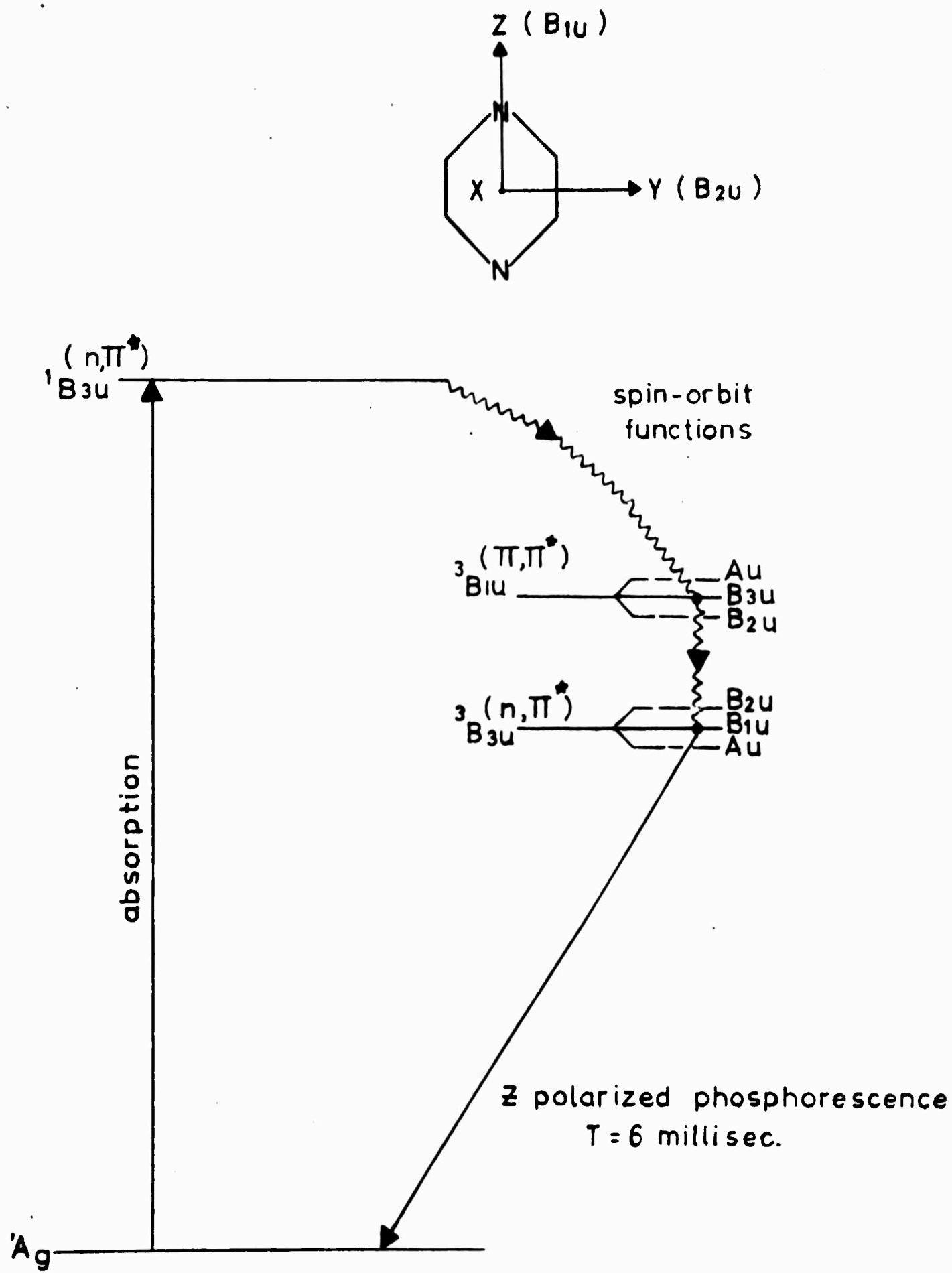


Fig. 2

DOCUMENT CONTROL DATA - R & D

Security classification of title, body, abstract and indexing, as determined by the entered when the overall report is classified)

| | | | |
|---|------------------------|--|--|
| 1. ORIGINATING ACTIVITY (Corporate author) | | 2. REFERENCE SECURITY CLASSIFICATION | |
| University of California, Los Angeles M. A. El-Sayed, Principal Investigator Los Angeles, California 90024 | | Unclassified | |
| 3. REPORT TYPE | | 4. GROUP | |
| SPIN POLARIZATION AND SPIN-LATTICE RELAXATION IN THE LOWEST TRIPLET STATE OF PYRAZINE AT 1.6°K | | none | |
| 5. DESCRIPTIVE NOTES (Type of report and inclusive dates) | | | |
| Technical Report | | | |
| 6. AUTHOR(S) (First name, middle initial, last name) | | | |
| M. A. El-Sayed, L. Hall, A. Armstrong, and W. R. Moomaw | | | |
| 7. REPORT DATE | 8a. TOTAL NO. OF PAGES | 8b. NO. OF REFS | |
| February, 1968 | 14 | 13 | |
| 9a. CONTRACT OR GRANTING | | 9b. ORIGINATOR'S REPORT NUMBER(S) | |
| Nonr-4756(07) | | | |
| b. PROJECT NO. ARPA Order No. 306 | | | |
| Task No. NR 015-816 | | | |
| c. | | 10. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| d. | | | |
| 11. DISTRIBUTION STATEMENT | | | |
| Distribution of this document is unlimited. | | | |
| 12. PRELIMINARY NOTES | | 13. SPONSORING MILITARY ACTIVITY | |
| | | Office of Naval Research Physics Branch Washington, D. C. | |
| 14. ABSTRACT | | | |
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| 14 KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Triplet state Spin-lattice relaxation Phosphorescence Pyrazine | | | | | | |